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(54) Title: LAUNDRY BAR COMPOSITIONS (57) Abstract The present invention is directed to built laundry bar compositions comprising a surfactant system which includes synthetic anionic surfactants and fatty acid soaps, and certain polyamine soil release agents to boost soil release performance while maintaining high sudsing.		

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LAUNDRY BAR COMPOSITIONS

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FIELD OF THE INVENTION

The present invention relates to laundry bar compositions with excellent,
10 sudsing, cleaning and soil suspending properties.

BACKGROUND OF THE INVENTION

Synthetic laundry bars typically comprise a synthetic anionic surfactant such as
the alkali metal salt of an alkylbenzene sulfonic acid or alkali metal salt of an alkyl
sulfate and one or more alkaline builders such as alkali metal polyphosphates,
15 carbonates or silicates. It is desired to remove a broad spectrum of soils and stains,
and dispersants in the bar formulation are useful in suspending polar, highly charged,
hydrophilic particles such as clay. At the same time, because the consumer of this type
of product usually associates good cleaning performance with high sudsing, it is
desirable to maintain high sudsing characteristics when formulating laundry bars.

20 It is an object of the invention to provide soap-based laundry bar compositions,
which provide superior sudsing, cleaning and soil suspending properties.

BACKGROUND ART

Patent Publication WO95/32272, published November 30, 1995, discloses the
use of alkoxylated, especially ethoxylated and/or propoxylated polyalkyleneamine
25 polymers as soil release agents in synthetic laundry bar products. The following
discloses various soil release polymers or modified polyamines: U.S. Patent 4,548,744,
Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1,
1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent
4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado,
30 et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May
16, 1995; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent
1,498,520, published January 18, 1978; German Patent DE 28 29 022, issued January
10, 1980; Japanese Kokai JP 06313271, published April 27, 1994.

SUMMARY OF THE INVENTION

35 The present invention is directed to laundry detergent bar compositions
comprising:

A. from about 1% to about 30% synthetic anionic surfactant;

- B. from about 10% to about 70% soap;
 C. from about 0.05% to about 3% soil release agent comprising a polyamine backbone corresponding to the formula:



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having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

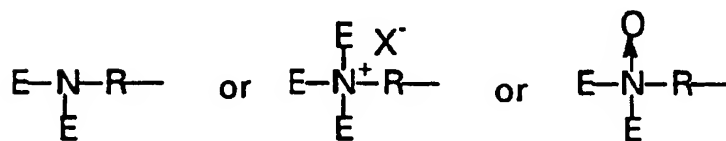


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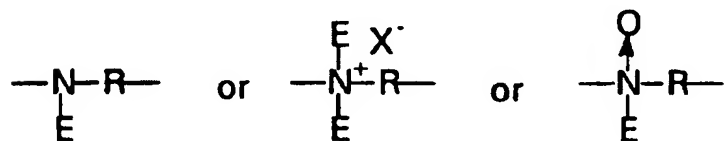
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

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- i) V units are terminal units having the formula:

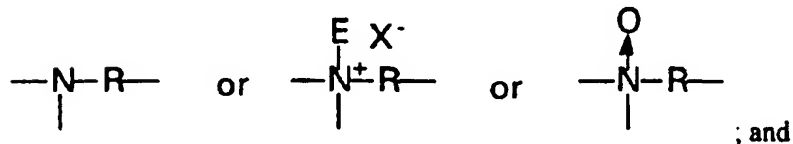


- ii) W units are backbone units having the formula:



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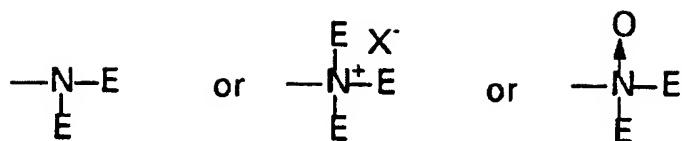
- iii) Y units are branching units having the formula:



- iv) Z units are terminal units having the formula:

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wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; oxide; B is hydrogen, C₁-C₆ alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and

- D. the balance adjunct ingredients, wherein the ratio of the synthetic anionic surfactant to soap is from about 1:50 to about 1:1.

DETAILED DESCRIPTION OF THE INVENTION

5 In accordance with the present invention it has been found that built laundry bars with excellent soil release performance, sudsing and cleaning performance can be achieved by using a surfactant system comprising synthetic anionic surfactant and soap with an effective amount of a polyamine soil release agent.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

As used herein, the term "alkyl" means a hydrocarbyl moiety which is straight or branched, saturated or unsaturated. Unless otherwise specified, alkyl are preferably saturated or unsaturated with double bonds, preferably with one or two double bonds.

15 The term "tallow" is used herein in connection with materials with fatty acid mixtures which typically are linear and have an approximate carbon chain length distribution of 2% C₁₄, 29% C₁₆, 23% C₁₈, 2% palmitoleic, 41% oleic, and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as those from palm oil and those derived from various animal tallow and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties.

The term "coconut oil" is used herein in connection with materials with fatty acid mixtures which typically are linear and have an approximate carbon chain length distribution of about 8% C₈, 7% C₁₀, 48% C₁₂, 17% C₁₄, 9% C₁₆, 2% C₁₈, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution in their fatty acids, such as palm kernel oil and babassu oil, are included within the term coconut oil.

Synthetic Anionic Surfactants

30 Synthetic anionic surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)
35 Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈₋₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and

the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C₁₁₋₁₃ LAS. The alkali metal salts, particularly the sodium salts of these surfactants are preferred. Alkylbenzene sulfonates and processes for making them are disclosed in U.S. Patent Nos. 2,220,099 and 2,477,383.

Other synthetic anionic surfactants suitable for use herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates. Preparation of alkyl glyceryl ether sulfonates are described in detail in U.S. Pat. 3,024,273, Whyte et al., issued March 6, 1962.

Another suitable surfactant for use herein are sodium or potassium salts of alkyl ethoxy ether sulfates (AES) having the following formula:



In the above structure R is alkyl of from about 10 to about 20 carbon atoms. On average, R is from about 13 to about 16. R is preferably saturated and linear.

In the above structure, x is an integer from 0 to about 20 and M is a water-soluble cation, for example, an alkali metal cation (e.g., sodium, potassium, lithium), preferably sodium or potassium, especially sodium.

The preferred AES surfactant has a saturated linear alkyl with an average of 14 to 15 carbon atoms, a range of from about 14 to about 15 carbon atoms, an average of about one ethoxy unit per molecule, and is a sodium salt (C₁₄₋₁₅AE₁Na).

In addition, suitable synthetic anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred synthetic anionic surfactants are C₁₀₋₁₈ linear alkylbenzene sulfonates, C₁₀₋₁₄ alkyl glyceryl ether sulfonates, and C₁₀₋₁₈ alkyl sulfates.

The amount of synthetic anionic surfactant in the composition herein is from about 1% to about 30%, preferably from about 2% to about 20%.

Soap

As used herein, "soap" means salts of fatty acids. The fatty acids are linear or branched containing from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms. The average carbon chain length for the fatty acid soaps is from about 12 to about 18 carbon atoms, preferably from about 14 to about 16 carbon atoms. Preferred salts of the fatty acids are alkali metal salts, such as sodium and potassium, especially sodium. Also preferred salts are ammonium and alkylammonium salts.

The fatty acids of soaps useful in the subject invention bars are preferably obtained from natural sources such as plant or animal esters; examples include coconut oil, palm oil, palm kernel oil, olive oil, peanut oil, corn oil, sesame oil, rice bran oil, cottonseed oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, grease, lard, and mixtures thereof. Preferred fatty acids are obtained from coconut oil, tallow, palm oil (palm stearin oil), palm kernel oil, and mixtures thereof. Fatty acids can be synthetically prepared, for example, by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.

Alkali metal soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

Preferred soap raw materials for the subject invention bars are soaps made from mixtures of fatty acids from tallow and coconut oil. Typical mixtures have tallow:coconut fatty acid ratios of 85:15, 80:20, 75:25, 70:30, and 50:50; preferred ratios are about 80:20 to 65:35.

Preferred soap raw materials for the subject invention are neat soaps made by kettle (batch) or continuous saponification. Neat soaps typically comprise from about 65% to about 75%, preferably from about 67% to about 72%, alkali metal soap; from about 24% to about 34%, preferably from about 27% to about 32%, water; and minor amounts, preferably less than about 1% total, of residual materials and impurities, such as alkali metal chlorides, alkali metal hydroxides, alkali metal carbonates, glycerin, and free fatty acids. Another preferred soap raw material is soap noodles or flakes, which are typically neat soap which has been dried to a water content of from about 10% to about 20%. The other components above are proportionally concentrated.

Soaps are present in the compositions herein at levels of from about 10% to about 70%, preferably from about 20% to about 50%. In the subject invention composition, the ratio of synthetic anionic surfactant to soap is from about 1:50 to

about 1:1, preferably from about 1:20 to about 1:1, more preferably from about 1:20 to about 1:4.

Soil Release Agent

- 5 The soil release agents of the present invention are water-soluble or dispersible, modified polyamines. The amount of polyamines in the composition herein is from about 0.05% to about 3%, preferably from about 0.3% to about 2%. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree.
- 10 In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

- For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by
- 15 oxidation or quaternization of at least one backbone nitrogen.
- 20

The linear or non-cyclic polyamine backbones that comprise the soil release agents of the present invention have the general formula:



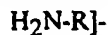
- 25 said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones comprising the soil release agents of the present invention have the general formula:



- 30 said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units.

For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

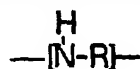


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



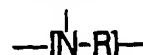
is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



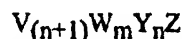
is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

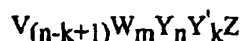


is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

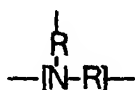
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



5 for linear polyamine soil release polymers and by the general formula

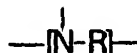


for cyclic polyamine soil release polymers. For the case of polyamines comprising rings, a Y' unit of the formula



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serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



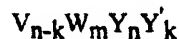
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that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula

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wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified

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polyamine according to the present invention has the formula



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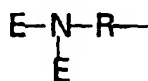
that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those

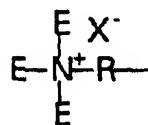
polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

a) simple substituted units having the structure:

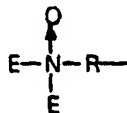


b) quaternized units having the structure:



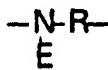
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

a) simple substituted units having the structure:

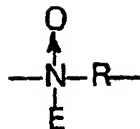


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

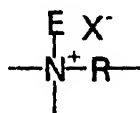


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- 5 a) unmodified units having the structure:



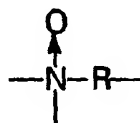
- b) quaternized units having the structure:



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wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:



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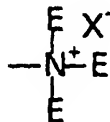
Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:



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- b) quaternized units having the structure:

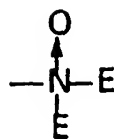


wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

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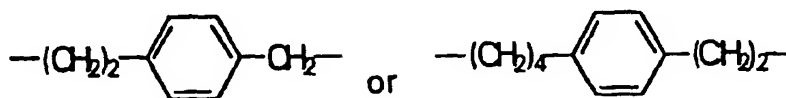


When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH₂CH₂)HN-

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula

25



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C₁₂ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise -(R¹O)_xR⁵(OR¹)_x-, CH₂CH(OR²)CH₂O)_z(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -CH₂CH(OR²)CH₂-, -(R¹O)_xR¹-, and mixtures thereof. Preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-,

CH₂CH(OR²)CH₂-, -(CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH-(OH)CH₂)_w-, -
 (R¹O)_xR⁵(OR¹)_x-, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxy-
 alkylene, C₄-C₁₂ dihydroxyalkylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-,
 (CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH-(OH)CH₂)_w-, and mixtures thereof, even
 5 more preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures
 thereof, most preferred are C₂-C₆ alkylene. The most preferred backbones of the
 present invention comprise at least 50% R units that are ethylene.

R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene. R²
 is hydrogen, and -(R¹O)_xB, preferably hydrogen.

10 R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkylene, C₇-C₁₂ alkyl substituted aryl, C₆-
 C₁₂ aryl, and mixtures thereof, preferably C₁-C₁₂ alkyl, C₇-C₁₂ arylalkylene, more
 preferably C₁-C₁₂ alkyl, most preferably methyl. R³ units serve as part of E units
 described herein below.

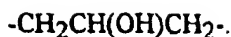
15 R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀
 arylene, preferably C₁-C₁₀ alkylene, C₈-C₁₂ arylalkylene, more preferably C₂-C₈
 alkylene, most preferably ethylene or butylene.

R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene,
 C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -C(O)(R⁴)_rC(O)-, -R¹(OR¹)-,
 -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, -C(O)(R⁴)_rC(O)-, -
 20 CH₂CH(OH)CH₂-, R⁵ is preferably ethylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -
 R¹(OR¹)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH-(OH)CH₂-,
 more preferably -CH₂CH(OH)CH₂-.

R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene.

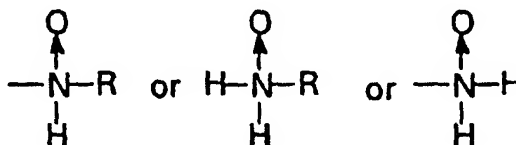
25 The preferred "oxy" R units are further defined in terms of the R¹, R², and R⁵
 units. Preferred "oxy" R units comprise the preferred R¹, R², and R⁵ units. The
 preferred soil release agents of the present invention comprise at least 50% R¹ units
 that are ethylene. Preferred R¹, R², and R⁵ units are combined with the "oxy" R units
 to yield the preferred "oxy" R units in the following manner.

- 30 i) Substituting more preferred R⁵ into -(CH₂CH₂O)_xR⁵(OCH₂CH₂)_x-
 yields -(CH₂CH₂O)_xCH₂CHOHCH₂(OCH₂CH₂)_x-.
- ii) Substituting preferred R¹ and R² into -(CH₂CH(OR²)CH₂O)_z-
 (R¹O)_yR¹O(CH₂CH(OR²)CH₂)_w- yields -(CH₂CH(OH)CH₂O)_z-
 35 (CH₂CH₂O)_yCH₂CH₂O(CH₂CH(OH)CH₂)_w-.
- iii) Substituting preferred R² into -CH₂CH(OR²)CH₂- yields

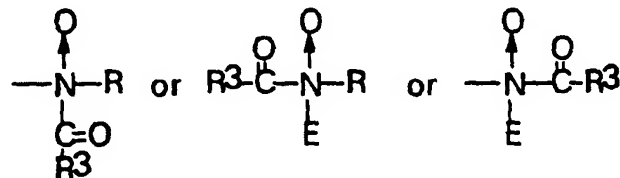


- E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-\text{CH}(\text{CH}_2\text{CO}_2\text{M})\text{CO}_2\text{M}$, $-(\text{CH}_2)_p\text{PO}_3\text{M}$, $-(\text{R}^1\text{O})_m\text{B}$, $-\text{C}(\text{O})\text{R}^3$, preferably hydrogen, C₂-C₂₂ hydroxyalkylene, benzyl, C₁-C₂₂ alkylene, $-(\text{R}^1\text{O})_m\text{B}$, $-\text{C}(\text{O})\text{R}^3$, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-\text{CH}(\text{CH}_2\text{CO}_2\text{M})\text{CO}_2\text{M}$, more preferably C₁-C₂₂ alkylene, $-(\text{R}^1\text{O})_x\text{B}$, $-\text{C}(\text{O})\text{R}^3$, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-\text{CH}(\text{CH}_2\text{CO}_2\text{M})\text{CO}_2\text{M}$, most preferably C₁-C₂₂ alkylene, $-(\text{R}^1\text{O})_x\text{B}$, and $-\text{C}(\text{O})\text{R}^3$.
- When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



- Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the E unit $-\text{C}(\text{O})\text{R}^3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

- B is hydrogen, C₁-C₆ alkyl, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q-(\text{CHSO}_3\text{M})\text{CH}_2\text{SO}_3\text{M}$, $-(\text{CH}_2)_q(\text{CHSO}_2\text{M})\text{CH}_2\text{SO}_3\text{M}$, $-(\text{CH}_2)_p\text{PO}_3\text{M}$, $-\text{PO}_3\text{M}$, preferably hydrogen, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-(\text{CH}_2)_q(\text{CHSO}_3\text{M})\text{CH}_2\text{SO}_3\text{M}$, $-(\text{CH}_2)_q-(\text{CHSO}_2\text{M})\text{CH}_2\text{SO}_3\text{M}$, more preferably hydrogen or $-(\text{CH}_2)_q\text{SO}_3\text{M}$.

- M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $-(\text{CH}_2)_p\text{CO}_2\text{M}$, and

$(\text{CH}_2)_q\text{SO}_3\text{M}$, thereby resulting in $-(\text{CH}_2)_p\text{CO}_2\text{Na}$, and $-(\text{CH}_2)_q\text{SO}_3\text{Na}$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(\text{CH}_2)_p\text{PO}_3\text{M}$ moiety substituted with sodium atoms has the formula $-(\text{CH}_2)_p\text{PO}_3\text{Na}_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

10 X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate (CH_3SO_3^-).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred soil release agents of the present invention comprise polyamine backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20% , more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred soil release agents which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are $\text{C}_2\text{-C}_{12}$ alkylene, preferred is $\text{C}_2\text{-C}_3$ alkylene, most preferred is ethylene.

The soil release agents of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the

polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

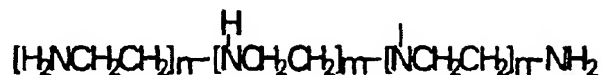
For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the soil release agents of the present invention.

Preferred soil release polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylpentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's

having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



- 5 wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

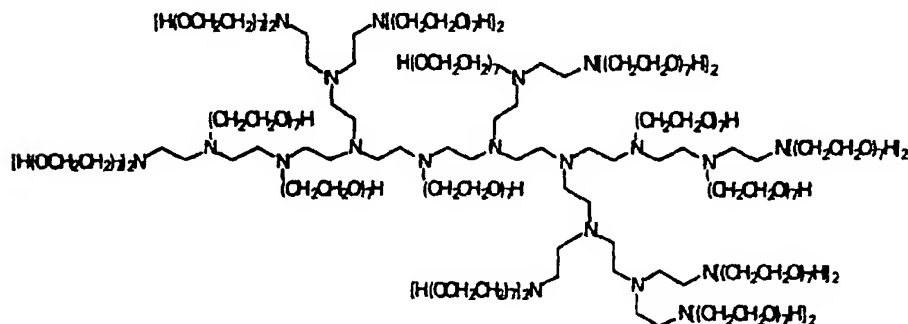
The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the
 10 polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing
 15 these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

20 Examples of modified soil release polymers of the present invention comprising PEI's, are illustrated in Formulas I - IV:

Formula I depicts a soil release polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, having the formula

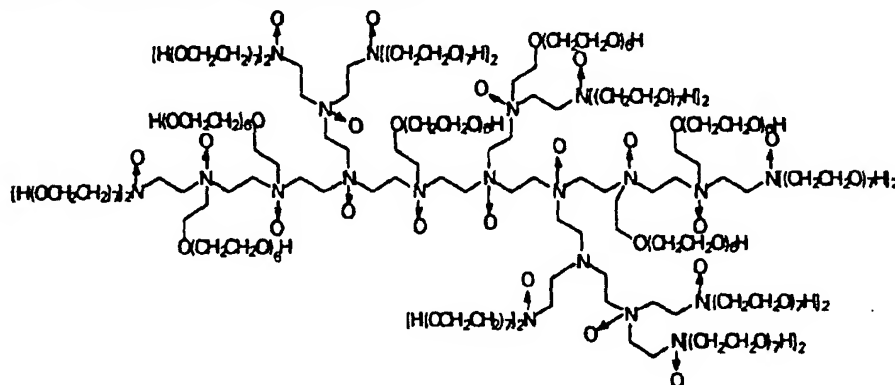
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Formula I

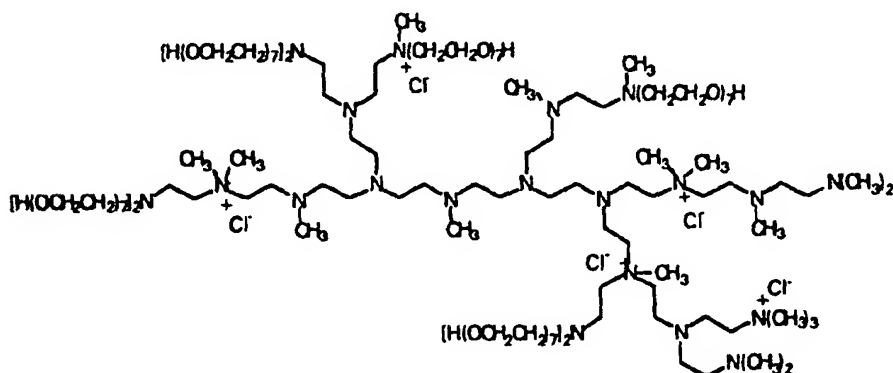
This is an example of a soil release polymer that is fully modified by one type of moiety.

Formula II depicts a soil release polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said soil release agent having the formula



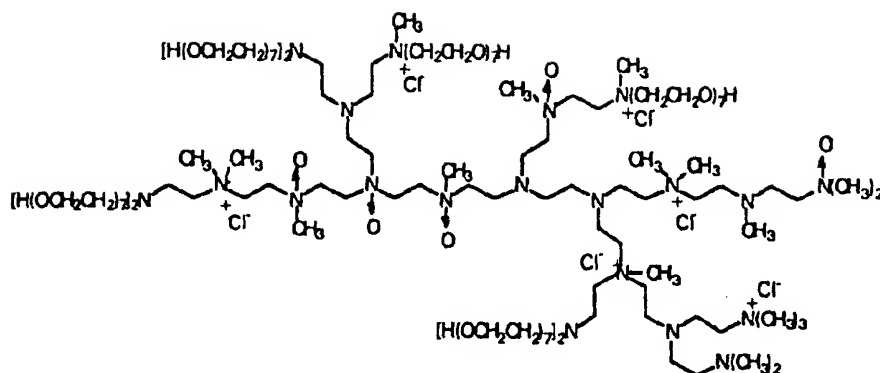
Formula II

Formula III depicts a soil release polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, or methyl groups. The modified PEI soil release polymer has the formula



Formula III

Formula IV depicts a soil release polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting soil release polymer has the formula



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

Adjunct Ingredients

Soil Suspending Agents

Soil suspending agents can be used. In the present invention, their use is balanced with the fabric softening clay/clay flocculating agent combination to provide optimum cleaning and fabric softening performance. One such soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan[®], from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof. A highly preferred soil suspending agent is a water-soluble salt of carboxymethylcellulose and carboxyhydroxymethylcellulose. Soil suspending agents should be used at levels up to about 5%, preferably about 0.1-1%.

Optional Surfactants

The detergent bars of the present invention can contain optional ingredients commonly used in detergent products. A typical listing of the classes and species of optional surfactants, (e.g. nonionic, zwitterionic and amphoteric surfactants) optional alkaline builders such as sodium carbonate trisodium phosphate sodium silicate, etc.

and other ingredients useful herein appears in U.S. Pat. No. 3,664,961, issued to Norris on May 23, 1972, and EP 550,652, published on April 16, 1992. Such optional surfactants, if present, can be included at levels up to a total of about 10%, preferably about 0.5-3%.

- 5 In addition, a hydrotrope, or mixture of hydrotropes, can be present in the laundry detergent bar. Preferred hydrotropes include the alkali metal, preferably sodium, salts of toluene sulfonate, xylene sulfonate, cumene sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope is added to the linear alkyl benzene sulfonic acid prior to its neutralization. The hydrotrope, if present, will preferably be
10 present at from about 0.5% to about 5% of the laundry detergent bar.

Moisture

The compositions of the subject invention comprise from about 5% to about 30% moisture, preferably from about 10% to about 25% moisture, more preferably from about 16% to about 25% moisture.

Builders

- The laundry bars of the invention can contain from about 0% to about 60%, preferably from about 5% to about 25% detergent builder. These detergent builders can be, for example, water-soluble alkali-metal salts of phosphate, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof.
20 Preferred builders are a water-soluble alkali-metal salt of tripolyphosphate, and a mixture of tripolyphosphate and pyrophosphate. The builder can also be a non-phosphate detergent builder. Specific examples of non-phosphate, inorganic detergency builders include water-soluble inorganic carbonate and bicarbonate salts. The alkali metal (e.g., sodium and potassium) carbonates, bicarbonates, and silicates
25 are particularly useful herein. Specific preferred examples of builders include sodium tripolyphosphates (STPP) and tetra sodium pyrophosphates (TSPP), and mixtures thereof. Other specifically preferred examples of builders include zeolites and polycarboxylates.

- Sodium carbonate is a particularly preferred ingredient in the subject invention
30 compositions, since in addition to its use as a builder, it can also provide alkalinity to the composition for improved detergency, and also can serve as a neutralizing agent for acidic components added in the composition processing. Sodium carbonate is particularly preferred as a neutralizing inorganic salt for an acid precursor of an anionic surfactant used in such compositions, such as the alkyl ether sulfuric acid and
35 alkylbenzene sulfonic acid.

Co-polymers of acrylic acid and maleic acid are preferred in the subject compositions as auxiliary builders, since it has been observed that their use in

combination with fabric softening clay and clay flocculating agents further stabilizes and improves the clay deposition and fabric softening performance.

Fabric Softening Clay

The fabric softening clay is preferably a smectite-type clay. The smectite-type
5 clays can be described as expandable, three-layer clays; i.e., aluminosilicates and
magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g.
of clay. Preferably the clay particles are of a size that they can not be perceived
tactilely, so as not to have a gritty feel on the treated fabric of the clothes. The fabric
softening clay can be added to the bar to provide about 1% to about 50% by weight of
10 the bar, more preferably from about 2% to about 20%, and most preferably about 3%
to 14%.

While any of the smectite-type clays described herein are useful in the present
invention, certain clays are preferred. For example, Gelwhite GP is an extremely
white form of smectite-type clay and is therefore preferred when formulating white
15 granular detergent compositions. Volclay BC, which is a smectite-type clay mineral
containing at least 3% iron (expressed as Fe_2O_3) in the crystal lattice, and which has a
very high ion exchange capacity, is one of the most efficient and effective clays for use
in the instant compositions from the standpoint of product performance. On the other
hand, certain smectite-type clays are sufficiently contaminated by other silicate
20 minerals that their ion exchange capacities fall below the requisite range; such clays
are of no use in the instant compositions.

Clay Flocculating Agent

It has been found that the use of a clay flocculating agent in a laundry bar
25 containing softening clay provides surprisingly improved softening clay deposition
onto the clothes and clothes softening performance, compared to that of laundry bars
comprising softening clay alone. The polymeric clay flocculating agent is selected to
provide improved deposition of the fabric softening clay. Typically such materials
have a high molecular weight, greater than about 100,000. Examples of such
30 materials can include long chain polymers and copolymers derived from monomers
such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate,
vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Gums, like guar gums, are
suitable as well. The preferred clay flocculating agent is a poly(ethylene oxide)
polymer. The amount of clay flocculating agent, if any, is about 0.2-2%, preferably
35 about 0.5-1%.

Other Optional Adjunct Ingredients

A particularly preferred optional component of the present invention is a detergent chelant. Such chelants are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof. The detergent chelant is particularly beneficial for maintaining good cleaning performance and improved surfactant mileage, despite the presence of the softening clay and the clay flocculating agent.

The detergent chelant is preferably a phosphonate chelant, particularly one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof.

Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1.

The detergent chelant can be included in the laundry bar at a level up to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, most preferably from about 0.5% to about 1.0%.

Another preferred additional component of the laundry bar is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. A preferred fatty alcohol has an alkyl chain predominantly containing from 16 to 18 carbon atoms, so-called "high-cut fatty alcohol," which can exhibit less base odor of fatty alcohol relative to broad cut fatty alcohols. Typically fatty alcohol, if any, is present in the laundry bar at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to a laundry bar as free fatty alcohol. However, low levels of fatty alcohol can be introduced into the bars as impurities or as unreacted starting material. For example, laundry bars based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

Another preferred optional component in the laundry bar is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred DTI ingredient can include polymeric DTI materials capable of binding fugitive dyes to prevent them from depositing on the fabrics, and

decolorization DTI materials capable of decolorizing the fugitives dye by oxidation. An example of a decolorization DTI is hydrogen peroxide or a source of hydrogen peroxide, such as percarbonate or perborate. Non-limiting examples of polymeric DTI materials include polyvinylpyrrolidone N-oxide, polyvinylpyrrolidone (PVP), PVP-
 5 polyvinylimidazole copolymer, and mixtures thereof. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") are also preferred for use herein. The amount of DTI included in the subject compositions, if any, is about 0.05-5%, preferably about 0.2-2%.

Another preferred optional component in the laundry bar is a secondary fabric
 10 softener component in addition to the softening clay. Such materials can be used, if any, at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and can include: amines of the formula $R_4R_5R_6N$, wherein R_4 is C_5 to C_{22} hydrocarbyl, R_5 and R_6 are independently C_1 to C_{10} hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula
 15 R_7COOH , wherein R_7 is C_9 to C_{22} hydrocarbyl, as disclosed in EP No. 0,133,804; complexes of such amines with phosphate esters of the formula $R_8O-P(O)(OH)-OR_9$ and $HO-P(O)(OH)-OR_9$, wherein R_8 and R_9 are independently C_1 to C_{20} alkyl of alkyl ethoxylate of the formula -alkyl-(OCH_2CH_2); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher
 20 alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827; and quaternary ammonium compounds of the formula $R_{10}R_{11}R_{12}R_{13}N^+X^-$, wherein R_{10} is alkyl having 8 to 20 carbons, R_{11} is alkyl having 1 to 10 carbons, R_{12} and R_{13} are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl^- or
 25 Br^- , such as C_{12-13} alkyl trimethyl ammonium chloride.

Yet another optional component in the laundry bar is a bleach component. The bleaching component can be a source of $-OOH$ group, such as sodium perborate monohydrate, sodium perborate tetrahydrate and sodium percarbonate. Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) is preferred since it has a dual function of both a
 30 source of $HOOH$ and a source of sodium carbonate. Another optional bleaching component is a peracid per se, such as a formula:



wherein z is from 2 to 4 and w is from 4 to 10. The bleaching component can contain, as a bleaching component stabilizer, a chelating agent of polyaminocarboxylic acids,
 35 polyaminocarboxylates such as ethylenediaminetetraacetic acid, diethylenetriaminopentaacetic acid, and ethylenediaminodisuccinic acid, and their salts with water-soluble alkali metals. The bleach components, if any, can be added to the

bar, if any, at a level up to 20%, preferably from about 1% to about 10%, more preferably from about 2% to about 6%.

Sodium sulfate is a well-known filler that is compatible with the compositions of this invention. It can be a by-product of the surfactant sulfation and sulfonation processes, or it can be added separately. Other filler materials include bentonite and talc.

Calcium carbonate (also known as Calcarb) is also a well known and often used filler component of laundry bars. Fillers include minerals, such as talc and hydrated magnesium silicate-containing minerals, where the silicate is mixed with other minerals, e.g., old mother rocks such as dolomite. Filler materials are typically used, if included, at levels up to 40%, preferably from about 5% to about 25%.

Binding agents for holding the bar together in a cohesive, soluble form can also be used, and include natural and synthetic starches, gums, thickeners, and mixtures thereof. Such materials, if included, are typically at levels up to about 3%, preferably about 0.5-2%.

Glycerine is commonly incorporated in laundry bar compositions. If included, it is typically at concentrations up to about 3%, preferably about 0.5-1.5%. Glycerine can affect bar brittleness.

Optical brighteners are also preferred optional ingredients in laundry bars of the present invention. Preferred optical brighteners are diamino stilbene, distyrylbiphenyl-type optical brighteners. Preferred as examples of such brighteners are 4,4'-bis[[4-anilino-6-bis(2-hydroxyethyl) amino-1,3,5-triazin-2-yl]amino]stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl) biphenyl and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt. Such optical brighteners, or mixtures thereof, can be used at levels in the bar of from about 0.05% - 1.0%.

Dyes, pigments, germicides, and perfumes can also be added to the bar composition. If included, they are typically at levels up to about 0.5%.

Another optional component of the subject invention composition is a photobleach material, particularly phthalocyanine photobleaches which are described in U.S. Patent 4,033,718 issued July 5, 1977, incorporated herein by reference. Preferred photobleaches are metal phthalocyanine compounds, the metal preferably having a valance of +2 or +3; zinc and aluminum are preferred metals. Such photobleaches are available, for example, under the tradename TINOLUS or as zinc phthalocyanine sulfonate. The photobleach components, if included, are typically in the subject compositions at levels up to about 0.02%, preferably from about 0.001% to about 0.015%, more preferably from about 0.002% to about 0.01%.

Another useful optional component of the subject compositions are detergent enzymes. Particularly preferred are cellulase, lipase, protease, amylase, and mixtures thereof. Enzymes, if included, are typically at levels up to about 5%, preferably about 0.5-3%.

5 The following are non-limiting examples of the synthesis of preferred soil release agents:

EXAMPLE I

Preparation of PEI 1800 E7

10 The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight
15 change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to about 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg
20 followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature,
25 and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exothermic. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole
30 ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74
35 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor

- the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed.
- 5 The mixture is further heated and agitated under vacuum for an additional 30 minutes.
- Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature,
- 10 and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exothermic. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.
- 15 The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the
- 20 reaction mixture while agitating and heating the mixture to 130 °C.

Example IA

Quaternization of PEI 1800 E₇

- To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added
- 25 polyethyleneimine having a molecular weight of 1800 which is further modified by ethoxylation to a degree of approximately 7 ethyleneoxy residues per nitrogen (PEI 1800, E₇) (207.3g, 0.590 mol nitrogen, prepared as in Example I) and acetonitrile (120 g). Dimethyl sulfate (28.3g, 0.224 mol) is added in one portion to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight.
- 30 The acetonitrile is removed by rotary evaporation at about 60 °C, followed by further stripping of solvent using a Kugelrohr apparatus at approximately 80 °C to afford 220 g of the desired partially quaternized material as a dark brown viscous liquid. The ¹³C-NMR (D₂O) spectrum obtained on a sample of the reaction product indicates the absence of a carbon resonance at ~58ppm corresponding to dimethyl sulfate. The ¹H-
- 35 NMR (D₂O) spectrum shows a partial shifting of the resonance at about 2.5 ppm for methylenes adjacent to unquaternized nitrogen has shifted to approximately 3.0 ppm. This is consistent with the desired quaternization of about 38% of the nitrogens.

Example II

Formation of amine oxide of PEI 1800 E₇

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added
5 polyethyleneimine having a molecular weight of 1800 and ethoxylated to a degree of
about 7 ethoxy groups per nitrogen (PEI-1800, E₇) (209 g, 0.595 mol nitrogen,
prepared as in Example I), and hydrogen peroxide (120 g of a 30 wt % solution in
water, 1.06 mol). The flask is stoppered, and after an initial exotherm the solution is
stirred at room temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a
10 sample of the reaction mixture indicates complete conversion. The resonances
ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the
original position at ~2.5 ppm to ~3.5 ppm. To the reaction solution is added
approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand
at room temperature for approximately 3 days. The solution is tested and found to be
15 negative for peroxide by indicator paper. The material as obtained is suitably stored as
a 51.1% active solution in water.

Example III

Formation of amine oxide of quaternized PEI 1800 E₇

20 To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added
polyethyleneimine having a molecular weight of 1800 which is further modified by
ethoxylation to a degree of about 7 ethyleneoxy residues per nitrogen (PEI 1800 E₇)
and then further modified by quaternization to approximately 38% with dimethyl
sulfate (130 g, ~0.20 mol oxidizable nitrogen, prepared as in Example II), hydrogen
25 peroxide (48 g of a 30 wt % solution in water, 0.423 mol), and water (~50 g). The
flask is stoppered, and after an initial exotherm the solution is stirred at room
temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a sample taken from
the reaction mixture indicates complete conversion of the resonances attributed to the
methylene peaks previously observed in the range of 2.5-3.0 ppm to a material having
30 methylenes with a chemical shift of approximately 3.7 ppm. To the reaction solution is
added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to
stand at room temperature for approximately 3 days. The solution is tested and found
to be negative for peroxide by indicator paper. The desired material with ~38% of the
nitrogens quaternized and 62% of the nitrogens oxidized to amine oxide is obtained
35 and is suitably stored as a 44.9% active solution in water.

EXAMPLE IV

Preparation of PEI 1200 E₇

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature,

and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

Other preferred examples such as PEI 1200 E15 and PEI 1200 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

EXAMPLE V

9.7% Quaternization of PEI 1200 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1200 ethoxylated to a degree of 7 (248.4g, 0.707 mol nitrogen, prepared as in Example 5) and acetonitrile (Baker, 200 mL). Dimethyl sulfate (Aldrich, 8.48g, 0.067 mol) is added all at once to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is evaporated on the rotary evaporator at ~60°C, followed by a Kugelrohr apparatus (Aldrich) at ~80°C to afford ~220g of the desired material as a dark brown viscous liquid. A ¹³C-NMR (D₂O) spectrum shows the absence of a peak at ~58ppm corresponding to dimethyl sulfate. A ¹H-NMR (D₂O) spectrum shows the partial shifting of the peak at 2.5ppm (methylenes attached to unquaternized nitrogens) to ~3.0ppm.

Processing

The detergent laundry bars of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of the

following key equipment: blender/mixer, mill or refining plodder, two- stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process the raw materials are mixed in the blender. Alkylbenzene sulfonic acid (when used) is added into a mixture of alkaline inorganic salts, strong electrolyte salts, and fillers (preferably including sodium carbonate) and the resulting partly neutralized mixture is mechanically worked to effect homogeneity and to complete the neutralization of the mixture. Once the neutralization reaction is completed, the soap, alkoxylated polymers, and any optional surfactants are added, followed by the builder and any additional optional components. If desired, polyphosphate can be used as an alkaline salt in the neutralization. The mixing can take from one minute to one hour, with the usual mixing time being from about two to twenty minutes. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyor.

After milling or preliminary plodding, the product is then conveyed to a double vacuum plodder, operating at high vacuum, e.g. 400 to 740 mm of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Examples of the invention are set forth hereinafter by way of illustration and are not intended to be in any way limiting of the invention.

EXAMPLE VI

Soap/synthetic laundry bars of the present invention, having the following compositions are prepared by conventional blending, milling and plodding procedures.

<u>Component</u>	<u>% Weight</u>			
Tallow Soap (Na)	16	30	30	30
Coconut Soap (Na)	16	7.5	8.0	7.5
Alkyl sulfate (Na)	12	7.7	0	4.6
Alkyl glyceryl ether sulfonate	0	0	2	0
AES (C45 E1 S)	0	0	0	2.25
Polyamine soil release agent of Example I	0.5	0.5	0.5	0.5
Na tripolyphosphate	5	0	0	0
Talc	17	30	30	30

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Carboxymethylcellulose	0.5	0	0.5	0.5
Sodium Carbonate	4	6	6	6
Moisture	15	17	17	17
Misc. Conventional Ingredients	Balance	Balance	Balance	Balance
TOTAL	100	100	100	100

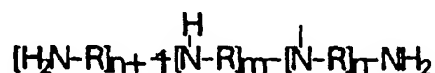
The bars have excellent cleaning and soil suspending properties and has better sudsing than a comparable bar that only contains synthetic anionic surfactant and no alkali metal soap of a fatty acid.

WHAT IS CLAIMED IS:

1. A laundry detergent bar composition comprising:
- from about 1% to about 30% synthetic anionic surfactant;
 - from about 10% to about 70% soap;
 - from about 0.05% to about 3% soil release agent comprising a

5

polyamine backbone corresponding to the formula:



having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

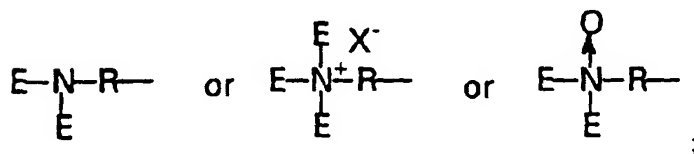
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having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

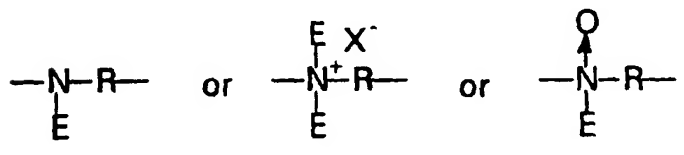
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- i) V units are terminal units having the formula:

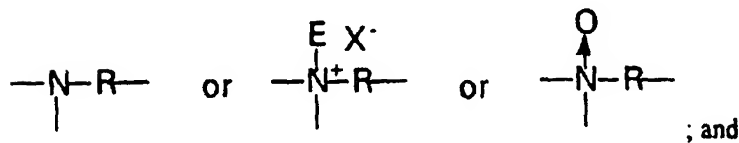


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- ii) W units are backbone units having the formula:

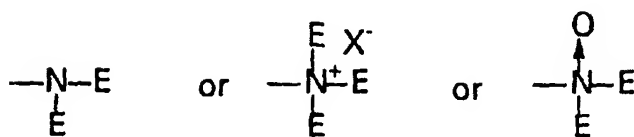


- iii) Y units are branching units having the formula:



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iv) Z units are terminal units having the formula:



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wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; oxide; B is hydrogen, C₁-C₆ alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the

- value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and
- 60 D. the balance adjunct ingredients, wherein the ratio of the synthetic anionic surfactant to soap is from about 1:50 to about 1:1.
2. A composition according to Claim 1, wherein R is C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, (R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OH)CH₂O)_z(R¹O)_yR¹-(OCH₂CH(OH)CH₂)_w-, -CH₂CH(OR²)CH₂-, and mixtures thereof.
 3. A composition according to Claim 2, wherein R is C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵-(OR¹)_x-, -(CH₂CH(OH)CH₂O)_z(R¹O)_yR¹-(OCH₂CH(OH)CH₂)_w-, and mixtures thereof.
 4. A composition according to Claim 3, further comprising 5% or less of a water-soluble salt of carboxymethylcellulose.
 5. A laundry detergent bar composition according to Claim 1, comprising:
 - A. from about 2% to about 20% synthetic anionic surfactant;
 - B. from about 20% to about 50% soap;
 - C. from about 0.3% to about 2% soil release agent; and
 - 5 D. the balance adjunct ingredients, wherein the ratio of the synthetic anionic surfactant to soap is from about 1:20 to about 1:1.
 6. A composition according to Claim 5, further comprising from about 0.1% to about 1% of a water-soluble salt of carboxymethylcellulose.
 7. A laundry detergent bar composition according to Claim 6, wherein the synthetic anionic surfactant is selected from the group consisting of alkali metal alkyl benzene sulfonates and alkyl sulfates.
 8. A composition according to Claim 7, wherein the synthetic anionic surfactant is alkylbenzene sulfonate surfactant and the soap is made from a mixture of fatty acids from tallow and coconut oil having a ratio of tallow:coconut fatty acid of from about 80:20 to about 65:35.
 9. A laundry detergent bar composition according to Claim 8, further comprising from about 5% to about 25% of an alkali metal polyphosphate selected from the group consisting of tripolyphosphate and pyrophosphate, and mixtures thereof.
 10. A method for providing soil release from fabric, said method comprising contacting fabric in need of cleaning with the laundry detergent bar composition of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/06273

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 6	C11D3/37	C11D3/40 C11D1/44 C11D1/40 C11D9/22
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC 6 C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 269 169 (PROCTER & GAMBLE) 1 June 1988 see page 3, line 22-25 see page 5, line 41-49 see page 5, last paragraph see page 6, line 41-42; claim 3 ---	1,5,7,9
A	WO,A,95 32272 (PROCTER & GAMBLE) 30 November 1995 cited in the application see page 8, line 19 - page 9, line 10 see page 9, line 22-30; claim 10 -----	1,5,7,9
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
18 December 1996		03.01.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer Van Bellingen, I

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/06273

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-269169	01-06-88	AU-A- 8143287	26-05-88
		DE-A- 3781101	17-09-92
		IE-B- 60696	10-08-94
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